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Zirconium bis-indenyl compounds. The influence of substituents on the ethene polymerization behavior of 1- and 2-substituted $(R\text{-}Ind)_2ZrCl_2$/MAO catalysts

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Abstract

A series of $[1\text{-}R\text{-}Ind]_2ZrCl_2$ (R = H, Me, Et, ^{i}Pr, ^{t}Bu, $SiMe_3$, Bz, Ph, 1-Naph) and $[2\text{-}R\text{-}Ind]_2ZrCl_2$ (R = Me, Et, $SiMe_3$, Bz, Ph) metallocenes were used in MAO co-catalyzed ethene polymerization reactions. The sizes of the ligands were measured from the perspective of the metal using the Tolman cone angle (θ), numerical solid angle and analytical solid angle measurement methods. Steric arguments permit an explanation of the polymerization activity between the different catalysts. The 1-substituted catalysts, in general were more active than their 2-substituted analogs, the difference becoming greater as the size of the R-group increased.

Keywords: Zirconium; Metallocenes; Indenyl ligands; Polymerization; Steric effects

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1. Introduction

Compared to the bridged bis-indenyl zirconocenes, which have proven to be outstanding catalysts for controlling propene tacticity [1], comparatively few research reports concerning the unbridged indenyl analogs have appeared in the open literature. This is because the untethered indenyl ligands are free to rotate, generally resulting in propene being polymerized in a non-stereospecific manner. However, Erker and co-workers has shown that placement of suitably bulky substituents, at the 1-position of the indenyl ligands, result in both stereoregular and atactic polymer being produced by the same catalyst [2,3]. This work was taken up further by Waymouth who revealed that the placement of bulky substituents at the 2-position of an indenyl ligand in unbridged $(Ind)_2ZrCl_2$ complexes yield a catalyst system that is capable of polymerizing propene into polypropylene containing sections of atactic and isotactic polypropylene, in the process forming a useful elastomeric polymer [4–16]. In their recent publications, Erker and co-workers [17–19] and Alt and co-workers [20,21] have developed this specific type of metallocene catalyst system further through their introduction of various heteroatom, alkyl and aryl groups at the 1- or 2-positions on the indenyl ligands.

The work presented in this paper entails a *systematic investigation* of the effect of alkyl, aryl and silyl substitution, at the C-1 and C-2 positions of the indenyl ligands, on the *ethene* polymerization behavior of a series of methylaluminoxane (MAO) catalyzed bis(indenyl)zirconium dichloride metallocenes of the formula: $(2\text{-}R\text{-}Ind)_2ZrCl_2$ [R = H (**1**), Me (**2**), Et (**4**), $SiMe_3$ (**8**), Ph (**10**), Bz (**12**) and 1-naphthyl (**14**)] and $(1\text{-}R\text{-}Ind)_2ZrCl_2$ [R = Me (**3**), Et (**5**), ^{i}Pr (**6**), ^{t}Bu (**7**), $SiMe_3$ (**9**), Ph (**11**), Bz (**13**) and 1-naphthyl (**15**)]. These alkyl and aryl substituents were chosen to cover a wide range of steric and electronic properties and our aim has been to determine a relationship, if any, between the electronic and steric properties of these substituents and metallocene polymerization activity. This paper also compares different steric measurement methods used to calculate the size of the substituted indenyl ligands.

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2. Results and discussion

2.1. Steric measurements

It is believed that the space occupied by the ligands surrounding the site (i.e. the zirconium atom) where polymerization takes place is crucial to the properties of the polymer produced. Hence, ligand size plays an important role in this respect. The ligand size can be quantified from the perspective of the zirconium to gauge the steric impact of the ligand environment on the active site using a number of methods. In this paper, we chose to measure the ligand size using the Tolman cone angle (θ) [22,23] the analytical solid angle (Ω) [24,25] and the numerical solid angle (Ω_N) methods [26]. The first two calculations have been employed in numerous studies that have appeared in the literature [24]. The measurement of Ω_N is shown in Fig. 1. This figure demonstrates how a *non-circular cone* is traced by rotating an axis through $\phi°$ thereby measuring the semi-cone angle, $\theta/2$, around the group being studied. This steric measurement can be expressed through Eq. (1):

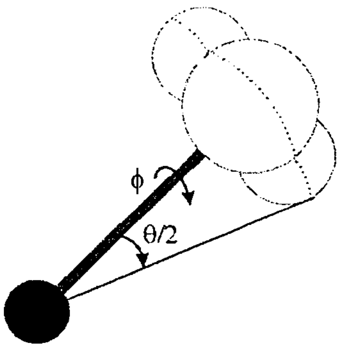

Fig. 1. Representation of the ligand angular profile used to create a non-circular cone.

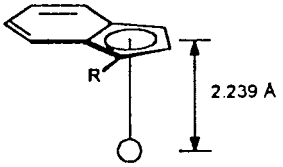

Fig. 2. The ligand sizes were measured from a point 2.239 Å from the indenyl ligand five-membered ring centroid (Cp_{cen}). This distance is equivalent to the average Zr–Cp_{cen} distance in 1- and 2-substituted bis(R-indenyl)zirconium dichloride metallocenes.

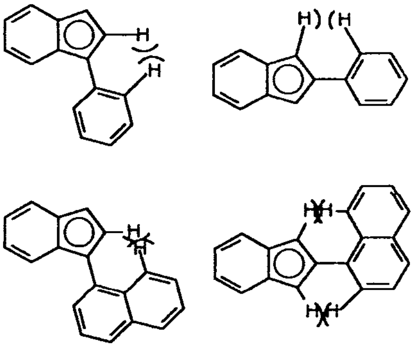

Fig. 3. Interaction of indenyl ligand substituents. In order to prevent steric conflicts as depicted in the diagram the aryl substituents were orientated such that they did not lie in the same plane as their parent indenyl ligands.

$$\Omega_N = \int_{\phi=0}^{2\pi} \left(1 - \cos\frac{1}{2}\theta\right) d\phi \qquad (1)$$

This calculation of Ω_N can be considered as a compromise between the measurement of 2 and Ω. Steric-measurements using these three methods were performed on metallocenes **1–15**. The calculations were done by measuring the size of the substituted indenyl ligands from a point 2.239 Å from the five-membered ring-centroid (Cp_{cen}) (Fig. 2). The distance chosen is equivalent to the average Cp_{cen}–Zr distance for similar metallocenes, determined from the Cambridge Structural Database (CSD).

Since no atomic coordinates are available for most of the metallocenes **1–15** (R-Ind)-M fragments were manually constructed. In doing so a number of assumptions were made as follows:

- Average bond distances, determined from X-ray crystallography and neutron diffraction studies [27,28], were used to construct the substituted indenyl ligands. Additional crystallographic data was obtained from selected structures [3–6,8,29,30] found in the CSD [31,32]. The Bondi data set of van der Waals radii was used in all the calculations [33].
- In order to minimize any unfavorable steric conflicts between the indenyl ligand and the phenyl and naphthyl substituents these were orientated such that they did not lie in the same plane (Fig. 3). In the original crystal structures, the dihedral angle formed by the phenyl ring to the indenyl ligand is 33 and 12° for the 1- and 2-substituted zirconium metallocenes, respectively [4,6,34]. As no crystal structure for the naphthyl substituted analogs exist, these parameters were also used in the construction of these fragments.
- The remaining ring substituents were placed on the five-membered ring so that the minimum ligand size was measured. It was assumed that non-bonded contacts between the growing polymer chain and the monomer coordinated to the metal would force the ring substituents into the above orientations to minimize steric interactions. In calculations of the so-called coordination gap aperture, Hortmann and Brintzinger did likewise in assessing the amount of space available for a metal-bound substrate molecule and the reaction complex [35,36]. Profiles of the fragments submitted to the steric calculation program are depicted in Fig. 4.

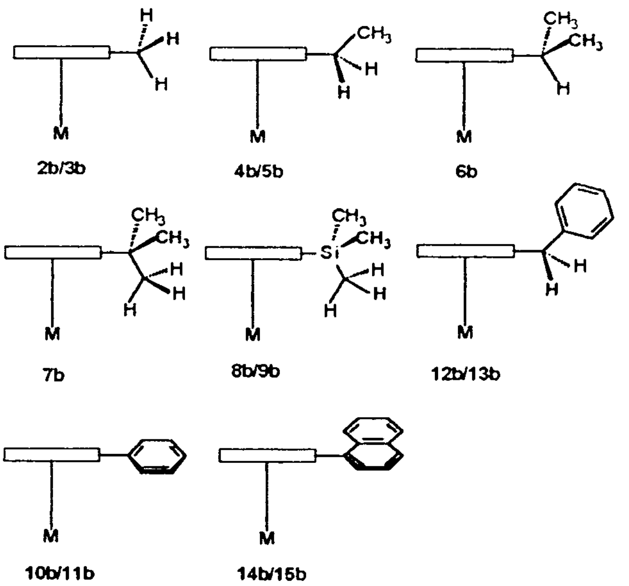

Fig. 4. Orientation of indenyl ligand substituents. The ring substituents were orientated in such a way to create a minimum steric interaction when the size of the substituted indenyl ligand was calculated from the perspective of the metal.

Table 1
Steric measurements for a set of 1- and 2-substituted (**R**-Ind)-M fragments [a]

R		Measurement technique [b]		
1-R	2-R	θ (°) [c]	Ω_N (°) [d]	Ω (°) [e]
H (**1**)		143	127	123
	Me (**2**)	150	135	131
Me (**3**)		150	135	130
	Et (**4**)	149	136	131
Et (**5**)		149	136	133
^{i}Pr (**6**)		152	138	134
^{t}Bu (**7**)		163	147	144
	$SiMe_3$ (**8**)	164	148	144
$SiMe_3$ (**9**)		163	147	144
	Ph (**10**)	150	139	134
Ph (**11**)		152	139	134
	Bz (**12**)	149	136	133
Bz (**13**)		149	136	132
	(1)-Naph (**14**)	150	140	136
(1)-Naph (**15**)		152	139	133

[a] The size of the R-Ind ligands was determined from the perspective of the metal.

[b] Errors (± 1°) are possibly due to small inaccuracies introduced during the construction of the ring fragments.

[c] The Tolman cone angle.

[d] The numerical solid angle.

[e] The solid angle calculated using analytical methods.

- The ring tilt observed in bis-indenyl Group 4 metallocenes was not taken into account and the origin point in the calculation (co-incidental with the metal atom) was placed at a point equidistant from all the indenyl ligand's five-membered ring carbon atoms. A comparison of the results from the steric calculations performed on the substituted cyclopentadienyl structures, which were performed on ring-tilted and non-tilted structures, revealed that there were no significant differences between these values [37].

The results from the calculations are presented in Table 1 and generally followed the expected trends with ligand size increasing: H > Me ~ Et ~ Bz > ^{i}Pr ~ Ph > 1-naphthyl > ^{t}Bu ~ $SiMe_3$.

The sizes measured for both the 1- and 2-substituted indenyl ligands are approximately the same in all three calculations. It is important to point out that although the 1- and 2-substituted indenyl ligands are similar in size, this has no bearing on the conformation they adopt with respect to each other in the solid state or in solution. This is clearly seen by comparing the crystal structures of the 1- and 2-phenyl substituted metallocenes. For the latter, two conformations are adopted in the solid state (Fig. 5A and B) [4,8], whereas in the former only one solid-state conformer is found (Fig. 5C) [34]. The conformations adopted by these metallocenes will be fully discussed in Section 2.2.

2.2. Polymerization studies

All the metallocene precatalysts employed in the polymerization studies were diastereomerically pure and were synthesized according to the literature procedures [4,34,38].

Individual polymerization reactions were performed under as near identical conditions as possible. However, due to the range of polymerization activities exhibited, it was necessary to adopt two sets of conditions to obtain a reliable activity series. In the first set of reactions, a low metallocene concentration (1.87×10^{-7} M) and high [Al]–[Zr] ratio (30 000:1) was employed (reaction conditions $\mathbf{P_A}$). Owing to the lower activity of some of the metallocenes and poor polymer yields obtained, it was necessary to complete a second set of polymerization reactions at higher metallocene concentrations (1.87×10^{-6} M, [Al]–[Zr] = 3000:1) (reaction conditions $\mathbf{P_B}$). Although different [Al]–[Zr] ratios were used for the two sets of polymerization conditions the amount of MAO co-catalyst remained the same. Employment of an [Al]–[Zr] ratio of 3000:1

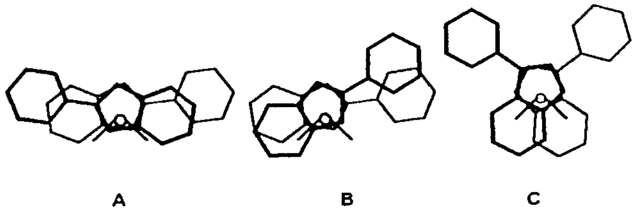

Fig. 5. Conformers of the $[2\text{-Ph-Ind}]_2ZrCl_2$ (**A** and **B**) and $[1\text{-Ph-Ind}]_2ZrCl_2$ (**C**) found in the solid state.

Table 2
Ethene polymerization data for a set of 1- and 2- substituted (**R**-Ind)$_2$ZrCl$_2$/MAO catalysts employing low metallocene concentrations [a]

No.	Catalyst		Activity ($\times 10^7$ g PE (mol Zr h)$^{-1}$) [b]	T_m (°C) [c]	M_w (g mol^{-1})	M_w/M_n
	1-R	2-R				
1	H (**1**)	H	5.87	129	554 000	3.1
2	Me (**3**)		2.34	130	535 600	2.6
3		Me (**2**)	1.17	130	334 500	2.4
4	Et (**5**)		2.13	131	248 300	2.0
5		Et (**4**)	0.64	131	782 400	4.6
6	^{i}Pr (**6**)		0.50	131		
7	SiMe$_3$ (**9**)		0.60	130	320 300	2.3
8	Ph (**11**)		2.64	129	577 600	3.1
9		Ph (**10**)	0.43	129	903 900	3.3
10	Bz (**13**) [d]		0.40	131	272 900	2.0
11	Bz (**13**)		0.57	131	462 700	3.7
12		Bz (**12**)	0.39	130	451 700	2.9

[a] Polymerization conditions: 400 ml toluene; mol Zr $= 7.5 \times 10^{-8}$ mol; [Al]–[Zr] $=$ 30 000:1; $T_p = 50$ °C; $P_p = 2$ bar; $t_p = 45$ min. All the metallocenes used in the polymerization reactor are the *rac*-diastereomers unless otherwise indicated (see [d]).

[b] Two to four polymerization reactions were performed for each metallocene listed in the table. The activity listed is the average value.

[c] Melting point determined by DSC analysis. These values have been obtained from the remelted samples at a heating rate of 10 °C min^{-1}.

[d] *meso*-Diastereomer.

Table 3
Ethene polymerization data for a set of 1- and 2- substituted (**R**-Ind)$_2$ZrCl$_2$/MAO catalysts employing high metallocene concentrations [a]

No.	Catalyst		Activity ($\times 10^6$ g PE (mol Zr h)$^{-1}$) [b]	T_m (°C) [c]	M_w (g mol^{-1})	M_w/M_n
	1-R	2-R				
13	^{i}Pr (**6**)		2.84	132	270 600	2.4
14	^{t}Bu (**7**)		0.32	130	398 400	6.7
15	SiMe$_3$ (**9**)		4.16	131	291 200	2.3
16		SiMe$_3$ (**8**)	0.37	131	385 200	5.7
17	Ph (**11**)		10.8	130	294 000	2.3
18		Ph (**10**)	2.38	130	345 700	2.3
19	Bz (**13**) [d]		2.97	131	450 200	3.2
20	Bz (**13**)		3.10	130		
21		Bz (**12**)	1.19	131	300 000	2.5
22	Naph (**15**) [d]		Traces	–	–	–

[a] Polymerization conditions: 400 ml toluene; mol Zr $= 7.5 \times 10^{-8}$ mol; [Al]–[Zr] $=$ 30 000:1; $T_p = 50$ °C; $P_p = 2$ bar; $t_p = 45$ min. All the metallocenes used in the polymerization reactor are the *rac*-diastereomers unless otherwise indicated (see [d]).

[b] Two to four polymerization reactions were performed for each metallocene listed in the table. The activity listed is the average value.

[c] Melting point determined by DSC analysis. Melting points were obtained from the remelted samples at a heating rate of 10 °C min^{-1}.

[d] *meso*-Diastereomer.

and a metallocene concentration of 1.87×10^{-7} M resulted in no observable polymerization activity. This concentration of MAO is thus below the minimum threshold required in our system to remove deleterious catalyst poisons. The results from the polymerization reactions and physical data on the polymer produced are shown in Tables 2 and 3.

The activities of the (1-R-Ind)$_2$ZrCl$_2$ and (2-R-Ind)$_2$ZrCl$_2$ metallocenes were found to decrease as follows:

- For the conditions $\mathbf{P_A}$ = H (**1**) > 1-Ph (**11**) > 1-Me (**3**) > 1-Et (**5**) > 2-Me (**2**) > 2-Et (**4**) > 1-SiMe$_3$ (**9**) > 1-^{i}Pr (**6**) ~ 2-Ph (**10**) ~ 1-Bz (**13**; *rac*) ~ 1-Bz (**13**; *meso*) ~ 2-Bz (**12**).
- For the conditions $\mathbf{P_B}$ = 1-Ph (**11**) > 1-SiMe$_3$ (**9**) > 1-Bz (**13**; *rac*) ~ 1-Bz (**13**-*meso*) > 1-^{i}Pr (**6**) > 2-Ph (**10**) > 2-Bz (**12**) > 2-SiMe$_3$ (**8**) > 1-^{t}Bu **7**) > 1-naphthyl (**15**; *meso*).

Steric effects associated with the ground state structures can be used to rationalize the polymerization activities of these metallocenes. Substituents equal to or greater in size than *iso*-propyl gave poor polymerization activity. In addition, the 1-substituted metallocenes generally displayed higher activities than their 2-substituted analogs. The latter point is illustrated by the observation that as the activity differences between these metallocenes becomes more pronounced, the larger is the substituent. For example, the methyl substituted metallocene **3** is only twice as active as **2**, but for the phenyl substituted metallocenes, this difference is sixfold. These steric effects can be understood by considering the ring conformations that the two indenyl ligands can adopt with respect to each other in the solid state.

An analysis of X-ray crystal structures of indenyl zirconium complexes has revealed that the ring substituents influence the conformation adopted by the rings in the solid state [3,17–19,34,39], as shown in Fig. 6. The crystal structures of metallocene **10** [4,8,40] show that it exists in two conformations while metallocene **11** [34] exists in one conformation suggesting that there are fewer restrictions to the conformational change in **10**.

It has been suggested by Fischer and Mülhaupt [1,41] as well as Kaminsky [42,43] that catalyst deactivation occurs through a bimolecular reduction process. Such deactivation processes can be prevented, or at least limited by certain ligand designs [44,45]. Comparing the conformations in the X-ray crystal structures of **10** (**A** and **B**, Fig. 5) and **11** (**C**), where **10** is significantly less active than **11**, we see that the annelated six-membered rings of the indenyl ligands in **11** provides better coverage of the active center. This coverage may limit the potential bimolecular deactivation pathways. The above arguments, based on solid-state studies are supported by solution ^{1}H-NMR spectroscopy studies [46–51]. For example, it is not possible to freeze out in solution any specific rotamer of (Cp^{t}Bu)$_2$ZrCl$_2$, even at − 100 °C. However, coordination of a modestly sized butadiene group in place of the two chloride atoms results in hindered rotation of the ligands. If we extend this result to a polymer bound metallocene, it is reasonable to presume that the bulky polymer chain will result in a higher rotational barrier for the ligands resulting in certain low energy conformer(s) being preferred. It is important to note here that Erker has recently remarked that unlike in the solid state, where pairs of conformers are found for this class of 1- and 2-substituted bis(indenyl)ZrCl$_2$ metallocene compounds [4,7,8], only a *single* favored rotamer is found in solution [17]. Indeed, Waymouth pointed out that the competition between any conformer in solution must be extremely subtle [7].

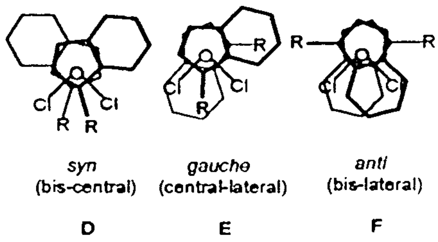

Fig. 6. Solid-state conformers adopted by Group 4 metallocenes with small (**D**, *syn*), intermediate (**E**, *gauche*) and large (**F**, *anti*) R-substituents [3,39].

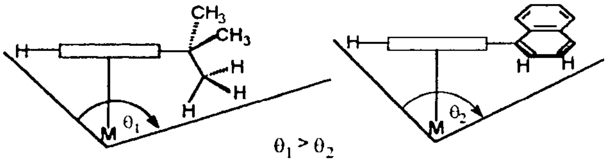

Fig. 7. Ligand orientations for **7** and **15**.

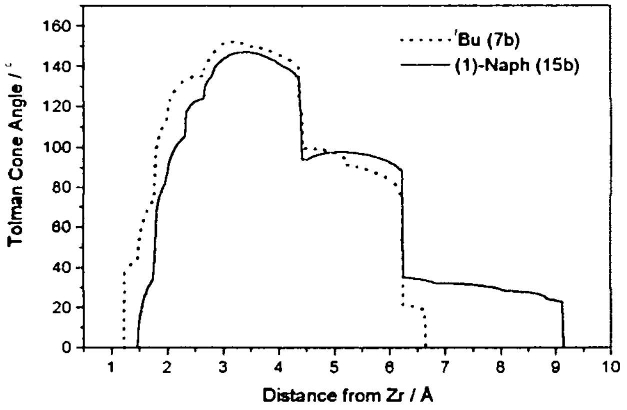

Fig. 8. Ligand profile plot showing the variation in ligand size as a function of distance from the zirconium metal.

The low activities recorded for the benzyl-substituted metallocenes, **12** and **13**, are unexpected. While our research was in progress, Lee observed similar low activities for **13** [52]. This could be related to an *intramolecular* coordination of the phenyl group to the cationic metal, resulting in an inhibition of the polymerization reaction. This phenomenon has been observed in the zirconocene complex, [(CpCMe$_2$Ph)(Cp)-ZrMe]$^+$[RB(C$_6$F$_5$)$_3$]$^-$ [53]. Likewise, the low activity of **7**, the *tert*-butyl substituted metallocene complex, could also result from intramolecular coordination of the *tert*-butyl group to the cationic metal. As before, precedence has been found for this in an analogous cyclopentadienyl zirconocene complex [54,55]. Although the *tert*-butyl and trimethylsilyl groups are similar in size, the trimethylsilyl-substituted indene **9** is 13 times more active than **7**. The larger silicon atom presumably places the methyl groups further away from the metal center, thereby precluding coordination to the active site. A similar interpretation has been proposed for polymerization studies involving mono-substituted bis(cyclopentadienyl)zirconium dichloride metallocenes [37].

All the steric calculations indicate that the ligands in the naphthyl-substituted catalyst **15** are smaller than those in the *tert*-butyl substituted catalyst **7** (Fig. 7). However, **15** was less active and produces only traces of the polymer. The ligand profile plots (Fig. 8) for these two ligands reveal that the naphthyl ligand extends further out in space and hence renders the active site less accessible to an approaching monomer. Interaction between the *tert*-butyl substituted ligand and the active site can be minimized by the ring substituent moving into a less restricted region around the metallocene complex, thereby providing greater access to the polymerization center.

Although we have been able to explain our results in terms of steric effects, electronic arguments must be considered. However, our attempts in finding a correlation using Hammet substituent parameters [56] proved unsuccessful. It will however be naïve to totally ignore the contribution of electronic factors, as it is likely that a combination of steric and electronic effects will be responsible for factors influencing catalyst activity and deactivation.

Both the *racemic* and *meso* diastereomers of **13** were tested for the polymerization activity. Both these metallocenes displayed almost identical ethene polymerization activity, with the *rac*-diastereomer being slightly more active. This result differs from the results obtained using propene in polymerization studies where large differences in activity between the two diastereomeric forms were observed [6,12,57].

Very little difference between the melting points of the polymers produced by these catalysts was observed and all lie in the narrow range of 129–132 °C. The only observable trend was a modest 1 °C increase in melting point on moving from polymerization conditions $\mathbf{P_A}$ to $\mathbf{P_B}$ (i.e. from the low to high concentration of the catalyst used in the polymerization reaction). These data are in keeping with a recent report by Jüngling and Mülhaupt where it was demonstrated that the *total* aluminum concentration is a more important parameter in influencing catalyst behavior than the [Al]–[Zr] molar ratio [58]. In our polymerization experiments, the aluminum concentration under conditions $\mathbf{P_A}$ and $\mathbf{P_B}$ was the same.

As has been observed in previous systems [1,42,59], the polymerization reactions carried out at lower concentrations of catalyst give rise to polymers with higher molecular weights (M_w). In addition, when the M_w of the 1- and 2-substituted ethyl (**4** and **5**), trimethylsilyl (**8** and **9**) and phenyl (**10** and **11**) complexes are compared, the 2-substituted catalysts give polymers with higher molecular weights. It has been demonstrated previously in propene polymerization reactions, albeit with ansa-metallocenes [44,45,60] that substituents at the 2-position limit β-hydride transfer to the olefin as a chain termination step. Presumably, the size of the substituents in our unbridged catalysts has an effect on the conformations adopted by the catalyst ligands in solution, with β-hydride transfer to an olefin hindered in the 2-substituted catalysts. The large polydispersities (M_w/M_n) and their range (2.0–6.7) point to multi-site catalysts. Similar findings have recently been reported by Alt when working on the same class of metallocene catalysts [20,21].

3. Conclusions

Ethene polymerization reactions performed with a series of 1- and 2-substituted bis(R-indenyl)zirconium dichloride (R = alkyl, aryl) metallocenes show that ground state steric effects can be used to rationalize the polymerization activity of the catalyst. The polymerization data reveal that a drop in reactivity occurs upon substitution of the indenyl ligand with simple alkyl group (methyl, ethyl and *iso*-propyl). Analyses of data from X-ray crystallographic studies suggest that the 1-substituted metallocenes are able to exist in conformations that limit bimolecular deactivation processes.

Thus, the design of a ligand system for use as an active polymerization catalyst requires that the active polymerization site be effectively protected from a reaction that leads to deactivation. This can be achieved by placing suitable bulky substituents at key positions on the ligands. However, if the ligands are too bulky, monomer access to the active site will be blocked and polymerization activity decreased.

4. Experimental

4.1. Steric measurements

Steric-measurements were performed on metallocenes **1**–**15**. The size of this ligand was determined from the perspective of the metal using the Tolman cone angle [22,23], analytical solid angle [24,25] and numerical solid angle methodologies [26]. The calculations were performed using the program STERIC, developed in our laboratories [61]. Calculations were performed in a Pentium 133 MHz PC running Red-Hat Linux 6.1.

4.2. General experimental procedures

All experimental procedures were carried out under inert air conditions, employing standard Schlenk techniques and apparatus. The metallocenes (**1**–**15**) employed in the polymerization reactions were synthesized according to the literature procedures [4,34,38]. Polymer melting points (m.p. (dec.)) were determined by Schümann-Sasol (Sasolburg, South Africa) and molecular weights by the Deutsche Kunststoffinstitut, Darmstadt.

4.3. Polymerization procedures

Experimental conditions for the polymerization reactions were selected so as to avoid diffusion limitations. Toluene was used as the solvent in all the polymerization reactions. The solvent was collected in a still-head after heating under reflux over molten sodium for 6 h. When fresh toluene was added to the still, its contents were heated under reflux for a minimum of 72 h prior to use in any polymerization reaction. Methylaluminoxane (MAO) was used as the co-catalyst in all the polymerization reactions and purchased from Witco as a 30% solution in toluene. The solvent was removed in vacuo at 30 °C from 20 ml quantities of this solution. The MAO was kept under vacuum for 5 h in total during this procedure to leave a glassy-white solid.

All polymerization reactions were carried out in a 1 l stainless-steel reactor, which was prepared before each polymerization by heating for 13 h at 80 °C under vacuum, cooling to 60 °C, and then filled with Ar. Under Ar counter-flow, 355 ml of toluene was added to the reactor via cannula tubing from a measuring cylinder. The reactor was then pressurized to 1 bar Ar pressure and allowed to equilibrate to the polymerization temperature of 50 °C. The required amount of MAO was added to an Schlenk tube, followed by 45 ml of toluene and the required amount of catalyst taken from a stock solution (made up by dissolving ca. 10 mg of metallocene in 20 ml of toluene). This mixture was allowed to age for 10 min at 50 °C and then added to the polymerization reactor via cannula tubing. The reactor was sealed, pressurized to 1 bar Ar pressure, and its contents stirred for 5 min. The polymerization reaction was then commenced by letting in ethene, at 2 bar pressure, to the reactor. The reaction was carried out for 45 min before termination by venting the reactor to the atmosphere and adding a solution of 10 ml 32% HCl in 90 ml methanol. The entire polymerization reactor contents were stirred at room temperature (r.t.) for 3 h before being collected by filtration onto a glass frit. The polymer was washed with methanol until no longer acidic and dried under reduced pressure to constant mass.

In the first set of reactions, a low metallocene concentration ($[\mathrm{Zr}] = 1.87 \times 10^{-7}$ mol l^{-1}) was employed together with a high [Al]–[Zr] ratio of 30 000:1 ($\mathbf{P_A}$). In the second set of polymerization reactions a tenfold increase in metallocene ($[\mathrm{Zr}] = 1.87 \times 10^{-6}$ mol l^{-1}) together with a lower [Al]–[Zr] ratio of 3000:1 ($\mathbf{P_B}$) was used. A minimum of two polymerization reactions was performed for each catalyst.

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